[19]中华人民共和国国家知识产权局

[51]Int. Cl⁷
C08L 63/00
B32B 15/08 B32B 33/00

[12]发明专利申请公开说明书

[21]申请号 00130490.9

[43]公开日 2001年5月2日

[11]公开号 CN 1293218A

[22]申请日 2000.10.12 [21]申请号 00130490.9

[30]优先权

[32]1999.10.13 [33]JP [31]291503/99

[32]2000.10.2 [33]JP [31]302070/00

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权利要求书2页 说明书14页 附图页数1页

[54]发明名称 环氧树脂组合物、粘性薄膜和预浸料坯及多层印刷电路板

[57]摘要

提供在导体电路层与绝缘层交互堆积的堆积方式多层印刷电路板中，绝缘层中不需要会使性能恶化的粗化成分就能形成粘合性优异的导体层的环氧树脂组合物，以及使用了该组合物的粘合性薄膜、预浸坯料多层印刷电路板及其制造法。所述环氧树脂组合物的必要成分是(A)1分子中有2个以上环氧基的环氧树脂、(B)苯酚系硬化剂、(C)有双酚S骨架、重均分子量为5000～100000的苯氧树脂和(D)硬化促进剂。

ISSN 1008-4274

知识产权出版社出版

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权利要求书

1．环氧树脂组合物，其必须成分为

（A）1分子中有2个以上环氧基的环氧树脂、

（B）苯酚系硬化剂、

（C）有双酚S骨架、重均分子量5,000～100,000的苯氧树脂，和

（D）硬化促进剂。

2．权利要求1记载的环氧树脂组合物，其中，环氧树脂（A）含有磷原子。

3．权利要求1或2记载的环氧树脂组合物，其中，苯酚系硬化剂（B）含有氮原子。

4．权利要求1～3记载的环氧树脂组合物，其特征在于苯氧树脂（C）具有双酚S骨架和联苯骨架，且重均分子量为5000～100000。

5．权利要求1～4记载的环氧树脂组合物，其中，相对于环氧树脂（A）和苯酚系硬化剂（B）的合计量100重量份而言，苯氧树脂（C）的配合量为5～50重量份，硬化促进剂（D）的配合量为0.05～10重量份。

6．粘合性薄膜，其特征在于在底基膜上形成权利要求1～5记载的环氧树脂组合物。

7．预浸料坯，其特征在于在纤维组成的片状增强基材上涂布和/或浸渍权利要求1～5记载的环氧树脂组合物。

8．多层印刷电路板，其特征在于在权利要求1～5记载的环氧树脂组合物的硬化物的糙化面上形成镀膜导体层，另一面粘合、层压在进行了图案加工的内层电路基板上。

9．多层印刷电路板，其特征在于在进行了图案加工的内层电路基板上涂布，加热硬化权利要求1～5记载的环氧树脂组合物，然后用氧化剂使该硬化物表面糙化，再通过镀膜在该糙化面上形成导体层。

10．多层印刷电路板，其特征在于在进行了图案加工的内层电路基板上，在加压、加热条件下层压权利要求6记载的粘合性薄膜，必要时剥离底基膜，使环氧树脂组合物加热硬化，然后用氧化剂使该硬化物表面糙化， 通过镀膜在该糙化面上形成导体层。

11．多层印刷电路板，其特征在于在进行了图案加工的内层电路

基板上，在加压、加热条件下层压、一体化权利要求 7 记载的预浸料坯，然后用氧化剂使该预浸料坯表面糙化，通过镀膜在该糙化面上形成导体层。

12．多层印刷电路板的制造方法，其特征在于在进行了图案加工的内层电路基板上涂布、加热硬化权利要求 1～5 记载的环氧树脂组合物，然后用氧化剂使该硬化树脂组合物表面糙化，再通过镀膜在该糙化面上形成导体层。

13．多层印刷电路板的制造方法，其特征在于在进行了图案加工的内层电路基板上，在加压、加热条件下层压权利要求 6 记载的粘合性薄膜，必要时剥离底基膜，使环氧树脂组合物加热硬化，然后用氧化剂使该硬化物表面糙化，再通过镀膜在该糙化面上形成导体层。

14．多层印刷电路板的制造方法，其特征在于在进行了图案加工的内层电路基板上，在加压、加热条件下层压、一体化权利要求 7 记载的预浸料坯，然后用氧化剂使该预浸料坯表面糙化，再通过镀膜在该糙化面上形成导体层。

15．层压板，它是通过将权利要求 1～5 记载的环氧树脂组合物涂布在两面铜张层压板的铜箔蚀刻面上或糙化（anchored）板的至少一面上，并加热硬化而得到的。

16．层压板，它是通过将权利要求 6 记载的粘合性薄膜在加压、加热条件下层压到两面铜张层压板的铜箔蚀刻面上或糙化板的至少一面上，必要时剥离底基薄膜，并加热硬化而得到的。

17．层压板，它是通过将权利要求 7 记载的预浸料坯在加压、加热条件下层压到两面铜张层压板的铜箔蚀刻面上或糙化板的至少一面上而得到的。

18．层压板，它是通过将权利要求 7 记载的预浸料坯在加压、加热条件下层压得到的。

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说 明 书

环氧树脂组合物、粘性薄膜和预浸料坯及多层印刷电路板

本发明涉及在导体电路层与绝缘层交互堆积的堆积方式（build-up）多层印刷电路板上兼备高耐热性和可用氧化剂糙化的层间绝缘材料用环氧树脂组合物，以及使用了该组合物的粘合性薄膜和预浸料坯，进一步涉及使用了这些的多层印刷电路板及其制造法。

近年来，作为多层印刷电路板的制造方法，在内层电路板的导体层上交互堆积有机绝缘层的堆积方式（build-up）制造技术引人瞩目。特开平 7－304931 号公报和特开平 7－304933 号公报中，公开了在形成了电路的内层电路板上涂布、加热硬化环氧树脂组合物，然后用糙化剂在表面上形成凸凹糙化面，再通过镀膜形成导体层的多层印刷电路板制造法。此外，在特开平 8－64960 号公报中，公开了涂布底涂粘合剂，初步干燥后贴合薄膜状添加剂粘合剂，加热硬化，用碱性氧化剂糙化，再通过镀膜形成导体层，来制造多层电路板的方法。在这些用途上使用的环氧树脂组合物中，作为硬化剂，一般是使用诸如双氰胺、咪唑化合物这样的胺系硬化剂。然而，近年来，随着实装密度的增大，即使在层压板同样、堆积方式的层间绝缘材料中，也希望有耐热性比先有技术优异的硬化体系。作为这样的问题的解决方法，我们已经在特开平 11－1547 号公报中开发了使用含有三嗪结构的苯酚系硬化剂、兼备高耐热性和可用氧化剂糙化性的层间绝缘材料用环氧树脂组合物。然而，该发明树脂组合物中必须有橡胶成分等糙化成分，因而在需要更微细的精细图案化、绝缘层薄膜化的领域中，耐热性或电绝缘性有时会成为问题。而且，最近从环境问题考虑，在使用引人瞩目的含磷原子环氧树脂代替溴系环氧树脂作为阻燃性环氧树脂的情况下，不能使现有树脂组合物得到良好的糙化面，也有其后的镀膜导体层剥离强度弱这样的问题。

本发明要解决的课题是开发兼备高耐热性和可用氧化剂糙化的层间绝缘材料用环氧树脂组合物，具体地说，没有橡胶成分等糙化成分，可以更微细的精细图案化，使绝缘层的薄膜化成为可能，使耐热性或电绝缘性良好，和改善其后的镀膜导体层剥离强度。

考虑到以上存在的问题，本发明者等人进行锐意研究，终于开发了在使用苯酚系硬化剂的系列中，不必使用糙化成分，就使采用氧化剂的糙化性成为可能的层间绝缘材料用环氧树脂组合物。

即，本发明的第1方面是以

（A）1分子中有2个以上环氧基的环氧树脂、

（B）苯酚系硬化剂、

（C）有双酚S骨架、重均分子量为5000～100000的苯氧树脂和

（D）硬化促进剂

为必须成分的环氧树脂组合物，尤其在环氧树脂（A）含有磷原子、苯酚系硬化剂（B）含有氮原子、苯氧树脂（C）有双酚S骨架和联苯骨架的情况下，是更适用的环氧树脂组合物；

第2方面，是本发明的环氧树脂组合物在底基薄膜上形成薄膜的粘性薄膜；

第3方面，纤维组成的片状增强基材中涂布、浸渍了该环氧树脂组合物的预浸料坯；第4方面，多层印刷电路板，其特征在于在该环氧树脂组合物的硬化层的糙化面形成镀膜导体层，另一面粘合层压到进行了图案加工的内层电路基板上；

第5方面，多层印刷电路板，其特征在于该环氧树脂组合物在进行了图案加工的内层电路基板上涂布、加热硬化后，用氧化剂使该组合物表面糙化，并通过镀膜在该糙化面上形成导体层；多层印刷电路板，其特征在于该粘性薄膜在加压、加热条件下层压到进行了图案加工的内层电路基板上，必要时剥离底基薄膜，使环氧树脂组合物加热硬化后，用氧化剂使该组合物表面糙化，并通过镀膜在该糙化面上形成导体层；以及多层印刷电路板，其特征在于该预浸料坯在加压、加热条件下层压到进行了图案加工的内层电路基板上，使之一体化之后，用氧化剂使该预浸料坯表面糙化，并通过镀膜在该糙化面上形成导体层；

第6方面，多层印刷电路板的制造法，其特征在于该环氧树脂组合物在进行了图案加工的内层电路基板上涂布、加热硬化后，用氧化剂使该组合物表面糙化，并通过镀在其糙化表面上形成导体层；多层印刷电路板的制造法，其特征在于该粘性薄膜在加压、加热条件下在进行了图案加工的内层电路基板上层压，必要时剥离底基薄膜，使环

氧树脂加热硬化后，用氧化剂使该组合物层表面糙化，并通过镀膜在其糙化面上形成导体层；以及该多层印刷电路板的制造法，其特征在于该预浸料坯在加压、加热条件下在进行了图案加工的内层电路基板上层压、一体化之后，用氧化剂使该预浸料坯表面糙化，并通过镀膜在该糙化面上形成导体层；以及

第 7 方面，层压板，是该环氧树脂组合物在两面铜张层压板的铜箔蚀刻面上或糙化板的至少一面上涂布、加热硬化而得到的；层压板，是该粘性薄膜在两面铜张层压板的铜箔蚀刻面上或糙化板的至少一面上在加压、加热条件下层压，必要时剥离底基薄膜，加热硬化而得到的；层压板，是该预浸料坯在两面铜张层压板的铜箔蚀刻面上或糙化板的至少一面上在加压、加热条件下层压而得到的；层压板，是预浸料坯在加压、加热条件下层压得到的。

本发明中使用的（A）成分，即 1 分子中有 2 个以上环氧基的环氧树脂，是得到足以作为层间绝缘材料的耐热性、耐药品性、电特性等诸物理性质所必需的。具体地说，可以使用双酚 A 型环氧树脂、双酚 F 型环氧树脂、双酚 S 型环氧树脂、苯酚线型酚醛树脂型环氧树脂、烷基苯酚线型酚醛树脂型环氧树脂、联苯酚型环氧树脂、萘型环氧树脂、二环戊二烯型环氧树脂、苯酚类与有酚羟基的芳香族醛的缩合物的环氧化物、异氰脲酸三缩水甘油酯、脂环式环氧树脂等众所周知的惯用品，可以单独使用，也可以 2 种以上组合使用。而且，也可以含有作为反应性稀释剂的单官能环氧树脂。

该环氧树脂（A）也可以含有磷原子。最近，代替上述环氧树脂的溴化物作为阻燃性环氧树脂，也可以使用引人注目的含磷原子环氧树脂。作为含磷原子环氧树脂，可以列举特开平 4－11662 号公报、特开平 11－166035 号公报中所公开的那些等。

本发明中使用的（B）成分，即苯酚系硬化剂，可以使用苯酚线型酚醛树脂，烷基苯酚线型酚醛树脂、双酚 A 线型酚醛树脂、二环戊二烯型酚醛树脂、Xylok 型酚醛树脂、萜烯改性酚醛树脂、聚乙烯基苯酚类等众所周知惯用品，可以单独使用，也可以 2 种以上组合使用。进而，苯酚系硬化剂（B）也可以含有氮原子。如果使用该苯酚系硬化剂，则可提高阻燃性和粘合性。作为有氮原子的苯酚系硬化剂，有含三嗪结构线型酚醛树脂、大日本油墨化学工业株式会社制フェノライト 7050

シリーズ、油化シエル（株）制三聚氰胺改性苯酚线型酚醛树脂等。关于上述酚醛树脂的配合量，希望相对于1环氧当量的环氧树脂（A）而言，配合0.5～1.3酚羟基当量的酚醛树脂。若在这个范围以外，则会产生使所得到的环氧树脂组合物的耐热性受损害这样的问题。

为了在加热硬化后达到采用氧化剂的良好糙化性，本发明中使用的（C）成分有双酚S骨架，重均分子量为5，000～100，000的苯氧树脂是必要的。进而，较好该苯氧树脂（C）有双酚S骨架和联苯骨架，且重均分子量为5，000～100，000。该苯氧树脂由于有砜基，因而与环氧树脂的相溶性差，虽然在环氧树脂组合物溶解于溶剂中而得到的清漆中是相溶的，但加热硬化后在环氧树脂硬化物中发生相分离而形成海岛结构。因此，使不添加糙化成分就能得到良好糙化面成为可能。若重均分子量不足5,000，则不能发挥相分离的效果；若超过100,000，则对有机溶剂的溶解性变差，而变得不能使用。作为该苯氧树脂，无论是使2官能环氧树脂与双酚S反应，还是使双酚S型环氧树脂与联苯酚反应等，都可以用众所周知的惯用方法进行。其中，在联苯型环氧树脂与双酚S组成的苯氧树脂的情况下，由于树脂本身的玻璃化温度高，因而有能得到致密糙化面这样的特征。关于这些苯氧树脂（C）的配合量，相对于环氧树脂（A）和苯酚系硬化剂（B）的合计量100重量份而言，在5～50重量份的范围内，可以根据其骨架选择最佳配合量。若不足5%（重量），则糙化性不能令人满意，而若超过50%（重量），则树脂清漆本身引起相分离，从而使硬化物的海岛构造逆转等，因而也不好。这些苯氧树脂由于可以提高硬化涂膜的机械强度和可挠性，因而在制作粘性薄膜和/或预浸料坯时也有容易进行树脂熔融粘度控制的效果，或防止沾粘的效果。而且，也可以组合使用通常的苯氧树脂、聚丙烯酸树脂、聚酰亚胺树脂、聚酰胺酰亚胺树脂、聚氰酸酯树脂、聚酯树脂、热固性聚苯醚树脂等粘合剂聚合物。

本发明中使用的（D）成分，即硬化促进剂，除咪唑类或叔胺类、胍类、或这些的环氧加合物或微胶囊化物外，还可以单独或2种以上组合使用三苯膦、四苯硼酸四苯鏻鎓等有机磷系化合物等众所周知的惯用品。关于这些硬化促进剂（D）的配合量，相对于环氧树脂（A）和苯酚系硬化剂（B）的合计量100重量份而言，较好的是在0.05～10重量份范围内。若少于0.05重量份，则硬化不足，而即使超过10重量

份，也不会再增大硬化促进效果，况且还会发生损害耐热性或机械强度的问题。本发明的第 1 方面，是相对于环氧树脂（A）和苯酚系硬化剂（B）的合计量 100 重量份而言，苯氧树脂（C）的配合量为 5～50 重量份、硬化促进剂的配合量为 0.05～10 重量份的环氧树脂组合物。

进而，本发明的环氧树脂组合物中，除上述成分外，还可以使用热固性树脂或众所周知的惯用添加剂。作为热固性树脂，可以列举嵌段异氰酸酯树脂、二甲苯树脂、自由基发生剂和聚合性树脂等。作为添加剂，可以使用诸如硫酸钡、钛酸钡、氧化硅粉、无定形硅石、滑石、粘土、云母粉、氢氧化铝、氢氧化镁等无机填料，硅酮粉、尼龙粉、氟树脂粉等有机填料、石棉、オルベン、ベントン等增粘剂，硅酮系、氟系、高分子系的消泡剂和/或流平剂，咪唑系、噻唑系、三唑系、硅烷偶合剂等的粘合性赋予剂，磷系阻燃剂等添加剂。而且，必要时还可以使用酞菁蓝、酞菁绿、碘绿、双偶氮黄、氧化钛、碳黑等众所周知的惯用着色剂。

本发明的第 2 方面，是在底基薄膜上形成环氧树脂组合物薄膜的粘性薄膜。作为制法，可以以底基薄膜为支撑体，在其表面上涂布该树脂组合物溶解于预定有机溶剂中得到的树脂清漆之后，通过加热和/或吹热风使溶剂干燥，来制作粘性薄膜。作为底基薄膜，可以列举聚乙烯、聚氯乙烯等聚烯烃，聚对苯二甲酸乙二醇酯等聚酯，聚碳酸酯，聚酰亚胺，以及脱模纸或铜箔、铝箔等金属箔等。要说明的是，对底基薄膜，除进行泥浆处理、电晕处理外，还可以实施脱模处理。作为有机溶剂，可以单独或 2 种以上组合使用通常溶剂，例如丙酮、甲乙酮、环己酮等酮类，乙酸乙酯、乙酸丁酯、乙酸溶纤素、乙酸丙二醇单甲醚酯、乙酸二甘醇一乙醚酯等乙酸酯类、溶纤素、丁基溶纤素等溶纤素类，Carbitol（二甘醇单乙醚乙酸酯，一种联合碳化物公司产品）、丁基 Carbitol 等 Carbitol 类，甲苯、二甲苯等芳香族烃类，以及二甲基甲酰胺、二甲基乙酰胺等。具体地说，在 10～200μm 厚的底基薄膜上，环氧树脂组合物层的厚度达到层压内层电路板的导体厚以上，即在 10～150μm 的范围内，并在树脂层的另一面上进一步层压 1～40μm 厚的支撑膜等保护薄膜，卷成辊筒状贮藏。

进而，本发明的第 3 方面，可以使该环氧树脂组合物用热熔体法或溶剂法涂布和/或浸渍到纤维组成的片状增强基材上，再进行加热、

半硬化，制作预浸料坯。作为纤维组成的片状增强基材，可以使用玻璃布或聚芳基酰胺纤维等众所周知的惯用预浸料坯用纤维。热熔体法，已知有使用无溶剂树脂组合物，一旦涂布到与树脂的剥离性好的涂布纸上就将其层压，或用口模式涂布机直接涂布无溶剂的树脂组合物的方法等。而溶剂法，有同粘性薄膜一样，在该环氧树脂组合物溶解于有机溶剂中得到的树脂清漆中浸渍、含浸片状增强基材，然后干燥而得到预浸料坯的方法。

以下涉及本发明的第 4 方面，即多层印刷电路板，其特征在于在该环氧树脂组合物层硬化物的糙化面上形成镀膜导体层，另一面粘合层压到进行了图案加工的内层电路基板上，并说明使用了这种环氧树脂组合物的多层印刷电路板的制造法。本发明的环氧树脂组合物涂布到进行了图案加工的内层电路基板上，在含有有机溶剂的情况下干燥后加热硬化。要说明的是，作为内层电路基板，可以使用玻璃环氧或金属基板、聚酯基板、聚酰亚胺基板、BT 树脂基板、热固性聚苯醚基板等，电路表面也可以进行预糙化处理。干燥条件较好在 70～130℃、5～40 分钟范围内，加热、硬化条件较好在 130～180℃、15～90 分钟范围内。加热硬化后，必要时在预定的表面孔、通孔部位等用钻和/或激光、等离子体进行打孔。然后，用高锰酸盐、重铬酸盐、臭氧、过氧化氢/硫酸、硝酸等氧化剂进行糙化处理，在粘合剂层表面上形成凸凹的锚。进而，通过电解和/或非电解镀膜，形成导体层，但此时所谓导体层既可以形成逆图案的镀膜保护层，也可以形成只有非电解镀膜的导体层。这样形成导体层之后，在 150～180℃进行 20～60 分钟退火处理，使残留的未反应环氧树脂硬化，也能进一步提高导体层的剥离强度。

关于本发明的第 6 方面，为了用本发明环氧树脂组合物和底基薄膜以及必要时还有保护薄膜组成的粘性薄膜制造多层印刷电路板，在进行了图案加工的内层电路基板上层压该粘性薄膜。层压品在有保护薄膜存在的情况下去掉保护薄膜之后，边加压、加热边贴合具有粘合剂性能的环氧树脂组合物薄膜。层压条件较好是，必要时使薄膜和内层电路基板预热，压粘温度是 70～130℃，压粘压力是 1～11 kgf/cm^2，在减压下层压。而且，层压既可以是间歇式的，也可以是连续辊压式的。层压后，冷却到室温附近时剥离支撑薄膜，使环氧树脂组合物转

印到内层电路基板上，然后加热硬化。此外，在使用实施了脱模处理的支撑薄膜的情况下，也可以在加热硬化后剥离支撑薄膜。然后，同上述方法一样用氧化剂使该薄膜表面糙化，通过镀膜形成导体层，就可以制造多层印刷电路板。

另一方面，为了用本发明环氧树脂组合物组成的预浸料坯制造多层印刷电路板，在进行了图案加工的内层电路基板上重叠 1 枚或必要时数枚该预浸料坯，经由脱模薄膜夹持金属平板，在加压、加热条件下加压层压。较好的是，压力条件为 5~40 kgf/cm^2，温度条件为 120~180 ℃，在 20~100 分钟范围内成形。此外，也可以按照以上所述层压方式制造。然后，同上述方法一样，用氧化剂使该预浸料坯表面糙化，通过镀膜形成导体层，就可以制造多层印刷电路板。所制造的多层印刷电路板，在内层电路基板有 2 层以上进行了图案加工的内层电路处于同一方向的情况下，该内层电路间便具有权利要求 1～5 的环氧树脂组合物的硬化物的绝缘层。本发明中所谓进行了图案加工的内层电路基板，是对于多层印刷电路板的相对称呼。例如，在基板两面上形成电路，进而，在该两电路表面上分别形成环氧树脂组合物的硬化薄膜作为绝缘层之后，进一步在该两表面上分别形成电路，就可以形成 4 层印刷电路板。这种情况下的内层电路基板，系指在基板上形成的两面上形成了电路的印刷电路板。进而，在这个 4 层印刷电路板的两表面上，如果进一步经由绝缘层分别追加形成一层电路，就可以得到 6 层印刷电路板。这种情况下的内层电路基板，系指所述 4 层印刷电路板。

关于本发明的第 5 方面，就是按照上述的本发明第 6 方面制造的多层电路板，即多层印刷电路板，其特征在于本发明的该环氧树脂组合物在进行了图案加工的内层电路基板上涂布、加热硬化后，用氧化剂使该硬化树脂组合物表面糙化，并通过涂膜在该糙化面上形成导体层；多层印刷电路板，其特征在于该粘性薄膜在进行了图案加工的内层电路基板上在加压、加热条件下层压，必要时剥离底基薄膜，使环氧树脂组合物加热硬化后，用氧化剂使该硬化树脂组合物表面糙化，并通过镀膜在该糙化面上形成导体层；多层印刷电路板，其特征在于该预浸料坯在进行了图案加工的内层电路基板上在加压、加热条件下层压、一体化之后，用氧化剂使该预浸料坯表面糙化，并通过镀膜在该糙化面上形成导体层。

本发明的第 7 方面涉及该环氧树脂组合物在两面铜张层压板的铜箔蚀刻面上或糙化板的至少一面上涂布、加热硬化得到的层压板；该粘性薄膜在两面铜张层压板的铜箔蚀刻面上或糙化板的至少一面上在加压、加热条件下层压，必要时剥离底基薄膜，加热硬化得到的层压板；该预浸料坯在两面铜张层压板的铜箔蚀刻面上或糙化板的至少一面上在加压、加热条件下层压得到的层压板；预浸料坯在加压、加热条件下层压得到的层压板，其制造方法说明如下。

本发明的环氧树脂组合物在两面铜张层压板的铜箔蚀刻面上或糙化板的至少一面上涂布、加热硬化，就可以得到层压板。

所述糙化（anchored）板是在铜张层压板制造时用脱模薄膜代替铜箔而得到的。这样得到的层压板，通过用高锰酸盐、重铬酸盐、臭氧、过氧化氢/硫酸、硝酸等氧化剂进行糙化处理，可以在层压板表面上形成凸凹锚状物，进而通过无电解和/或电解镀膜，可以在层压板表面上直接形成导体层。

又，本发明的环氧树脂组合物组成的粘性薄膜在两面铜张层压板的铜箔蚀刻面上或糙化板的至少一面上层压、加热硬化，可以得到层压板。这样得到的层压板，通过用高锰酸盐、重铬酸盐、臭氧、过氧化氢/硫酸、硝酸等氧化剂进行糙化处理，可以在层压板表面上形成凸凹锚状物，进而通过无电解和/或电解镀膜，可以在层压板表面上直接形成导体层。

又，本发明的环氧树脂组合物组成的预浸料坯以预定枚数重叠，或放在两面铜张层压板的铜箔蚀刻面上或糙化板的至少一面上，经由脱模薄膜夹持金属平板，在加压、加热条件下进行加压层压，可以得到层压板。这样得到的层压板，通过用高锰酸盐、重铬酸盐、臭氧、过氧化氢/硫酸、硝酸等氧化剂进行糙化处理，可以在层压板表面上形成凸凹锚状物，进而通过无电解和/或电解镀膜，可以在层压板表面上直接形成导体层。

实施例

以下显示制造例、实施例和比较例，具体地说明本发明，但本发明不限定于此。

实施例 1

作为（A）成分的双酚 A 型环氧树脂（环氧当量 185，油化 Shell

Epoxy 公司制“エピコート 828”）20 重量份（以下配合量全部用重量份表示）、甲酚线型酚醛环氧树脂（环氧当量 215，大日本油墨化学工业公司制“エピクロン N－673”）45 份和作为（B）成分的苯酚线型酚醛树脂（酚羟基当量 105，大日本油墨化学工业公司制“フェノライト”）30 份，边搅拌边加热溶解于乙酸二甘醇单乙醚酯 20 份、溶剂石脑油 20 份中，冷却到室温后，向其中添加作为（C）成分的 828 和双酚 S 组成的苯氧树脂的环己酮清漆（油化 Shell Epoxy 公司制“YL 6747 H 30”，不挥发分 30％（重量），重均分子量 47000）30 份和作为（D）成分的 2－苯基－4, 5－二（羟甲基）咪唑粉碎品 0.8 份，进一步添加微细粉碎硅石 2 份、硅酮系消泡剂 0.5 份，制作了环氧树脂组合物。

实施例 2

作为（A）成分的双酚 A 型环氧树脂（油化 Shell Epoxy 公司制“エピコート 828”）20 份、特开平 11－166035 号公报记载的合成例 1 的含磷环氧树脂（环氧当量 300、磷含量 2.0％重量）45 份，边搅拌边加热溶解于甲乙酮（以下简称 MEK）中，冷却到室温后，向其中添加作为（B）成分的有三嗪结构的苯酚线型酚醛树脂的 MEK 清漆（大日本油墨化学工业公司制“フェノライト LA－7052”，不挥发分 60％，不挥发分的酚羟基当量 120）50 份、作为（C）成分的四甲基型的联苯酚型环氧树脂（油化 Shell Epoxy 公司制“YX－4000”）和双酚 S 组成的苯氧树脂的环己酮清漆（油化 Shell Epoxy 公司制“YL 6746 H 30”，不挥发分 30％（重量），重均分子量 30000）70 份、作为（D）成分的 2, 4－二氨基－6－（2－甲基－1－咪唑基乙基）－1, 3, 5－三嗪·异氰脲酸盐粉碎品 0.5 份，进一步添加微细粉碎硅石 2 份，制作了环氧树脂组合物。这种清漆状环氧树脂组合物用辊涂机涂布在厚度 38μm 的 PET 薄膜上，使之干燥后的厚度达到 60μm，在 80～120℃干燥 10 分钟，得到粘性薄膜。

实施例 3

作为（A）成分的甲酚线型酚醛环氧树脂（大日本油墨化学工业公司制“エピクロン N－673”）15 份、特开平 11－166035 号公报记载的合成例 1 的含磷环氧树脂（环氧当量 300，磷含量 2.0％（重量））50 份，边搅拌边加热溶解于 MEK 中，冷却到室温后，向其中添加作为（B）

成分的有三嗪结构的苯酚线型酚醛树脂的 MEK 清漆（大日本油墨化学工业公司制“フェノライト LA－7052”）45 份、作为（C）成分的四甲基型的联苯酚型环氧树脂和双酚 S 组成的苯氧树脂的环己酮清漆（油化 Shell Epoxy 公司制“YL 6746 H 30”）50 份、作为（D）成分的 2, 4－二氨基－6－（2－甲基－1－咪唑基乙基）－1, 3, 5－三嗪·异氰脲酸盐粉碎品 0.5 份；进一步添加苯氧树脂清漆（东都化成公司制“YP－50－EK35”）20 份、微细粉碎硅石 2 份，制作了环氧树脂组合物。让这种清漆状环氧树脂组合物含浸到聚芳基酰胺纤维布（帝人公司“テクノーラ”）中，在 150℃干燥，得到树脂含量 45％（重量）左右、厚度 0.1mm 的预浸料坯。

实施例 4

实施例 2 记载的环氧树脂组合物浸渍到 100μm 的玻璃布中，在 80～120℃干燥 10 分钟，得到树脂含量 40％的预浸料坯。

实施例 5

实施例 2 记载的环氧树脂组合物浸渍到 34μm 的玻璃布中，在 80～120℃干燥 10 分钟，得到树脂含量 75％的预浸料坯。

比较实施例 1

作为（A）成分的双酚 A 型环氧树脂（油化 Shell Epoxy 公司制“エピコート 828”）20 重量份、甲酚线型酚醛环氧树脂（大日本油墨化学工业公司制“エピクロン N－673”）45 份、作为（B）成分的苯酚线型酚醛树脂（大日本油墨化学工业公司制“フェノライト”）30 份，边搅拌边加热溶解于乙酸二甘醇单乙醚酯 20 份、溶剂石脑油 20 份中，冷却到室温后，向其中添加苯氧树脂清漆（东都化成公司制“YP－50－EK35”）30 份和作为（D）成分的 2－苯基－4, 5－二（羟甲基）咪唑粉碎品 0.8 份，进一步添加微细粉碎硅石 2 份、硅酮系消泡剂 0.5 份，制作了环氧树脂组合物。

比较实施例 2

作为（A）成分的双酚 A 型环氧树脂（油化 Shell Epoxy 公司制“エピコート 828”）20 份、特开平 11－166035 号公报记载的合成例 1 的含磷环氧树脂（环氧当量 300、磷含量 2.0％（重量））45 份，边搅拌边加热溶解于 MEK 中，冷却到室温后，向其中添加作为（B）成分的有三嗪结构的苯酚线型酚醛树脂的 MEK 清漆（大日本油墨化学工

业公司制“フェノライト LA－7052”）50 份，进一步添加末端环氧化聚丁二烯橡胶（ナガセ化成工业公司制“デナレックス R－45 EPT”）15 份、碳酸钙 15 份、苯氧树脂清漆（东都化成公司制“YP－50－EK 35”）30 份、作为（D）成分的 2，4－二氨基－6－（2－甲基－1－咪唑基乙基）－1，3，5－三嗪·异氰脲酸盐粉碎品 0.5 份、微细粉碎硅石 2 份，制作了环氧树脂组合物。这种清漆状环氧树脂组合物用辊涂机涂布到厚度 38μm 的 PET 薄膜上，使之干燥后的厚度达到 60μm，在 80～120℃干燥 10 分钟，得到粘性薄膜。

制造例 1

从铜箔 35μm 的玻璃环氧两面铜张层压板制作内层电路基板，用丝网印刷法涂布实施例 1 得到的环氧树脂组合物，在 120℃干燥 10 分钟后，里面也以同样方式涂布、干燥，在 170℃加热硬化 30 分钟。然后，在预定的表面孔、通孔部位等用钻和/或激光进行打孔，然后用高锰酸盐碱性氧化剂（アトテックジャパン公司制药液）对该树脂层表面进行糙化处理后，进行无电解和/或电解镀膜，按照 Subtractive 法得到 4 层印刷电路板。然后，进一步在 170℃加热 30 分钟，进行退火处理。

制造例 2

从铜箔 35μm 的玻璃环氧两面铜张层压板制作内层电路基板，用真空层压机，在温度 110℃、压力 1 kgf/cm²、气压 5mmHg 以下的条件下两面层压实施例 2 得到的粘性薄膜，然后剥离 PET 薄膜，在 170℃加热硬化 30 分钟。然后，在预定的表面孔、通孔部位等用钻和/或激光进行打孔，然后用高锰酸盐的碱性氧化剂对该薄膜表面进行糙化处理，进行无电解和/或电解镀膜，按照 Subtractive 法得到 4 层印刷电路板。然后，进一步在 150℃进行 30 分钟退火处理。

制造例 3

从铜箔 35μm 的玻璃环氧两面铜张层压板制作内层电路基板，两面各重叠 1 枚实施例 3 得到的预浸料坯，经由脱模薄膜夹持金属平板，在 120℃以 10 kgf/cm² 加压层压 15 分钟后，在 170℃以 40kgf/cm² 加压层压 60 分钟。然后，在预定的表面孔、通孔部位等用钻和/或激光进行打孔，然后用高锰酸盐的碱性氧化剂对表面进行糙化处理，通过全面进行无电解和/或电解镀膜形成导体层后，按照 Subtractive 法得到 4 层印刷电路板。

00·10·12

比较制造例 1

用比较实施例 1 得到的环氧树脂组合物，同制造例 1 完全一样进行，得到 4 层印刷电路板。

比较制造例 2

用比较实施例 2 得到的环氧树脂组合物，同制造例 2 完全一样进行，得到 4 层印刷电路板。

对于制造例 1～3 和比较制造例 1～2 得到的 4 层印刷电路板，糙化后的树脂表面电子显微镜（SEM）照片显示于图 1 中，进而，导体剥离强度测定和煮沸耐热性的结果列于表 1 中。

〔表 1〕

	剥离强度（kgf/cm）	煮沸耐热性
制造例 1	0.90	O
制造例 2	1.1	O
制造例 3	1.0	O
比较制造例 1	0.25	×
比较制造例 2	0.30	×

剥离强度测定：按照 JIS C6481 进行。导体镀膜厚约 30μm。

煮沸耐热性：对于所得到的 4 层印刷电路板，2 小时煮沸处理后在 260℃的焊锡浴中浸渍 30 秒钟，进行评价。评价是通过目视判定各该试验基板的外观进行的。

O，良好；×起泡、剥落或ミーズリング发生。

从实施例 1～3、制造例 1～3 的结果可以看出，按照本发明的方法，通过用氧化剂糙化可以形成粘合性优异的铜镀膜，而且兼备高耐热性，因此，用堆积方式（build - up）可以制造可靠性高的多层印刷电路板。尤其在环氧树脂（A）含有磷原子、苯酚系硬化剂（B）含有氮原子、苯氧树脂（C）有双酚 S 骨架和联苯骨架的情况下，可以判明，除剥离强度高外，还能糙化形成更致密的锚状物，因而适用于精细图案。另一方面，在不含有本发明必须（C）成分的比较实施例 1 中，用氧化剂不能形成充分发挥锚效果的凸凹状态，因而铜镀膜的剥离强度低。此外，像比较实施例 2 那样，在使用含有磷原子的环氧树脂的情况下，即使含有糙化成分，糙化形状也差，铜镀膜的粘合性低，因而煮沸耐热性差，得不到耐实用的制品。

制造例 4

对铜箔 18μm 的玻璃环氧两面铜张层压板的铜箔进行蚀刻，两面各重叠一枚实施例 5 得到的预浸料坯，经由脱模薄膜，用真空层压机在温度 110℃、压力 1 kgf/cm²、气压 5mmHg 以下的条件下两面层压后，剥离脱模薄膜，在 170℃加热硬化 60 分钟，得到了层压板。然后用高锰酸钾的碱性氧化剂进行表面糙化处理，全面进行无电解和/或电解镀膜，形成约 30μm 的导体层。

其剥离强度是 1.0 kgf/cm 。

制造例 5

实施例 4 得到的预浸料坯 2 枚重叠，经由脱模薄膜用金属平板夹持，在 120℃、10kgf/cm² 加压层压 15 分钟后，在 170℃、40kgf/cm² 加压层压 60 分钟，得到板厚 0.2mm 的层压板。此层压板的特性列于表 2 中。然后用高锰酸钾的碱性氧化剂进行表面糙化处理，全面进行无电解和/或电解镀膜，形成约 30μm 的导体层。

其剥离强度是 0.9 kgf/cm 。

表 2

特性		层压板
CTE（ppm）	x-y	10.6
	z	56
介电常数	1MHz	4.81
	500MHz	4.4
	1GHz	4.37
介电损耗角正切	1MHz	0.026
	500MHz	0.023
	1GHz	0.022
抗张强度（kgf/mm²）		27.4
破断伸长率（%）		2.8
挠曲强度（kgf/mm²）	纵向	49
	横向	50.3
挠曲弹性模量（kgf/mm²）	纵向	1749
	横向	1930

按照本发明的方法，在堆积方式多层印刷电路板的制造中，适合于精细图案的形成，而且绝缘层中不需要会使性能恶化的糙化成分就能形成粘合性优异的导体层。

下面简单说明附图

图 1 是 4 层印刷电路板糙化后的树脂表面电子显微镜（SEM）照片。制造例 1 得到的 SEM 照片显示于图 1 的 a 中，制造例 2 的显示于同图的 b 中，制造例 3 的显示于同图的 c 中，比较制造例 1 的显示于同图的 d 中，比较制造例 2 显示于同图的 e 中。

说 明 书 附 图

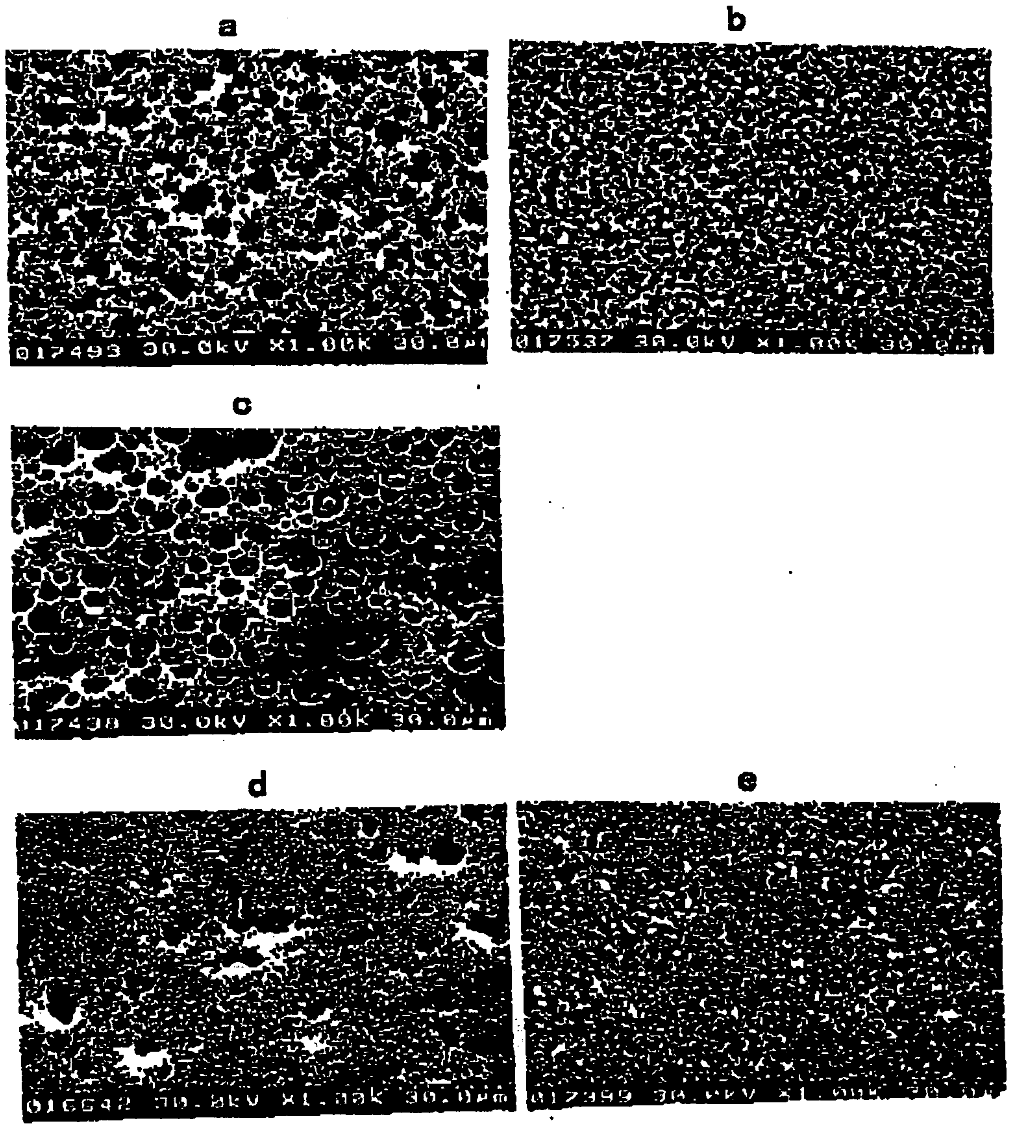


图 1

DF4378/PCT/US/B-915

VERIFICATION OF A TRANSLATION

I, the below named translator, hereby declare:

That my name is Masao SHIMOKOSHI;

That my address is No. 356-46, Obayashi, Koshigaya-shi, Saitama-ken, 343-0021 Japan;

That I know well both the English and Japanese languages:

That I translated the patent document: CN 1293218A published on May 2, 2001 into the English language; and

That the attached English language translation is a true and correct translation of the said patent document to the best of my knowledge and belief.

Date: April 29, 2005

Masao Shimokoshi

Masao SHIMOKOSHI

DF4347/B-675

SPECIFICATION

TITLE OF THE INVENTION

Epoxy Resin Composition, and Adhesive Film and Prepreg Using the Composition, and Multilayer Printed-wiring Board Using them, and Process for Manufacturing the Same

BACKGROUND OF THE INVENTION

[Industrial Field of the Invention]

The present invention relates to an epoxy resin composition for an interlayer insulating material in a multilayer printed-wiring board of the build-up type which is formed by stacking alternately conductor circuitry layers and insulating layers, the cured product of the composition exhibiting both high thermal resistance and capability of being roughened with an oxidizing agent. It also relates to an adhesive film and a prepreg made by using the composition, a laminate and a multilayer printed-wiring board made by using them, and a process for manufacturing the same.

[Prior Art]

As a process for manufacturing a multilayer printed-wiring board, attention has recently been focused on the build-up type technique wherein an organic insulating layer is formed alternately on a conductor layer of an internal-

layer circuit board. Japanese Patent Application Laid-Open (Kokai) Nos. 304931/1995 and 304933/1995 disclose a process for manufacturing a multilayer printed-wiring board which process comprises the steps of coating an internal-layer circuit board having a circuit formed thereon with an epoxy resin composition, curing it under heating, forming an unevenly roughened surface thereon with a roughening agent and forming a conductor layer by plating. And, Japanese Patent Application Laid-Open (Kokai) No. 64960/1996 also discloses a process for manufacturing a multilayer printed-wiring board which process comprises the steps of applying an undercoat adhesive, drying it preliminarily, bonding an additive adhesive in the film form thereto, curing it under heating, roughening it with an alkaline oxidizing agent and forming a conductor layer by plating. As a curing agent for the epoxy resin composition used for these purposes, an amine-type curing agent such as dicyandiamide, an imidazole compound or the like has been generally used. With the recent increase of real loading density, however, similarly to the laminate type, a curing system exhibiting stronger thermal resistance as compared with a conventional system is desired for an interlayer insulating material of the build-up type. As a method for solving such a problem, the inventors have developed an epoxy resin composition for an interlayer insulating material exhibiting both high thermal resistance and capability of being roughened with an oxidizing agent using a phenolic curing agent containing a

triazine structure as shown in Japanese Patent Application Laid-Open (Kokai) No. 1547/1999. However, the resin composition of the present invention essentially necessitates a roughening component such as rubber component, the thermal resistance or electric insulation has sometimes come into question in the fields where a finer pattern or a thinner insulating layer is required. Furthermore, in the case where an epoxy resin containing a phosphorus atom which attracts attention as a flame retardant epoxy resin, is used instead of a bromine-type epoxy resin from the viewpoint of recent environmental problems, there exists the problem that a conventional resin composition does not afford any well-roughened surface and therefore, peeling strength of the resulting plated conductor layer is poor.

SUMMARY OF THE INVENTION

[Problems to be Solved by the Invention]

Therefore, it is an object of the present invention to develop an epoxy resin composition for an interlayer insulating material exhibiting both high thermal resistance and capability of being roughened with an oxidizing agent, more particularly, an epoxy resin composition which is capable of giving a finer pattern and making an insulating layer thinner, the cured product of which exhibits good thermal resistance and electric insulating property, and improves peeling strength of the resulting plated conductor

layer.

Other objects and advantages of the present invention will be apparent from the following description, drawings, and disclosure.

[Means for Solving the problems]

In view of the aforementioned problems, the present inventors have studied intensively and succeeded in developing an epoxy resin composition for an interlayer insulating material capable of being roughened with an oxidizing agent without necessitating a roughening component in a system of using a phenolic curing agent, on the basis of which the present invention has been made.

Namely, a first embodiment of the present invention relates to an epoxy resin composition comprising, as the essential components, (A) an epoxy resin having two or more epoxy groups in one molecule, (B) a phenolic curing agent, (C) a phenoxy resin containing a bisphenol S skeleton and having a weight average molecular weight of 5,000 to 100,000, and (D) a curing accelerator.

Particularly, preferred is the epoxy resin composition wherein the epoxy resin (A) contains a phosphorus atom, the phenolic curing agent (B) contains a nitrogen atom, and the phenoxy resin (C) contains a bisphenol S skeleton and a biphenyl skeleton.

A second embodiment of the present invention relates to an adhesive film which is obtainable by forming a thin

film of the epoxy resin composition of the present invention on a supporting base film.

A third embodiment of the present invention relates to a prepreg which is obtainable by coating and/or impregnating a sheet-shape reinforced base material made of a fiber with the above-described epoxy resin composition.

A fourth embodiment of the present invention relates to a multilayer printed-wiring board wherein a plated conductor layer is formed on the roughened surface of a cured product of the above-described epoxy resin composition and the other surface is closely laminated onto a patterned internal-layer circuit board.

A fifth embodiment of the present invention relates to a multilayer printed-wiring board which is obtainable by the steps of coating a patterned internal-layer circuit board with the above-described epoxy resin composition, curing it under heating, roughening the surface of the cured product with an oxidizing agent, and forming a conductor layer on the roughened surface by plating;

a multilayer printed-wiring board which is obtainable by the steps of laminating the above-described adhesive film on a patterned internal-layer circuit board under conditions of pressurizing and heating, detaching the supporting base film, if necessary, curing the epoxy resin composition under heating, roughening the surface of the cured composition layer with an oxidizing agent, and forming a conductor layer on the roughened surface by plating; and

a multilayer printed-wiring board which is obtainable by the steps of laminating the above-described prepreg on a patterned internal-layer circuit board under conditions of pressurizing and heating to integrate them, roughening the surface of the prepreg with an oxidizing agent, and forming a conductor layer on the roughened surface by plating.

A sixth embodiment of the present invention relates to a process for manufacturing a multilayer printed-wiring board comprising the steps of coating a patterned internal-layer circuit board with the above-described epoxy resin composition, curing it under heating, roughening the surface of the cured composition with an oxidizing agent, and forming a conductor layer on the roughened surface by plating;

a process for manufacturing a multilayer printed-wiring board comprising the steps of laminating the above-described adhesive film on a patterned internal-layer circuit board under conditions of pressurizing and heating, detaching the supporting base film, if necessary, curing the epoxy resin composition under heating, roughening the surface of the cured product layer with an oxidizing agent, and forming a conductor layer on the roughened surface by plating; and

a process for manufacturing a multilayer printed-wiring board comprising the steps of laminating the above-described prepreg on a patterned internal-layer circuit

board under conditions of pressurizing and heating to integrate them, roughening a surface of the prepreg with an oxidizing agent, and forming a conductor layer on the roughened surface by plating.

A seventh embodiment of the present invention relates to a laminate which is obtainable by the steps of coating a surface formed by etching out a copper foil of a copper foil-clad laminate on both sides or at least one surface of an unclad laminate with the above-described epoxy resin composition, and curing it under heating;

a laminate which is obtainable by the steps of laminating the above-described adhesive film on a surface formed by etching out a copper foil of a copper foil-clad laminate on both sides or at least one surface of an unclad laminate under conditions of pressurizing and heating, detaching the supporting base film, if necessary, and curing it under heating;

a laminate which is obtainable by laminating the above-described prepreg on a surface formed by etching out a copper foil of a copper foil-clad laminate on both sides or at least one surface of an unclad plate under conditions of pressurizing and heating; and

a laminate which is obtainable by laminating the above-described prepreg under conditions of pressurizing and heating.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows SEM photographs of the cured resin surfaces after roughening with regard to four-layer printed-wiring boards. Figure 1a shows an SEM photograph of the roughened surface obtained in Manufacturing Example 1; Figure 1b, that in Manufacturing Example 2; Figure 1c, that in Manufacturing Example 3; Figure 1d, that in Comparative Manufacturing Example 1; and Figure 1e, that in Comparative Manufacturing Example 2.

DETAILED DESCRIPTION OF THE INVENTION

The epoxy resin having two or more epoxy groups in each molecule, which is to be used as the component (A) according to the present invention, is necessary for attaining an interlayer insulating material having sufficiently high levels of physical properties, such as thermal resistance and chemical resistance, and electrical properties. More specifically, it is possible to use one of known and commonly used resins such as a bisphenol A type epoxy resin, a bisphenol F type epoxy resin, a bisphenol S type epoxy resin, a phenol novolak type epoxy resin, an alkylphenol novolak type epoxy resin, a biphenyl type epoxy resin, a naphthalene type epoxy resin, a dicyclopentadiene type epoxy resin, an epoxidated product of a condensation product of a phenol and an aromatic aldehyde having phenolic

hydroxyl group(s), triglycidyl isocyanurate, and an alicyclic epoxy resin, or a combination of two or more of the above epoxy resins. It may contain a monofunctional epoxy resin as a reactive diluent.

The epoxy resin (A) may contain a phosphorus atom. 0006
It is possible to use an epoxy resin containing a phosphorus atom which recently attracts attention as a flame retardant epoxy resin. The epoxy resin containing a phosphorus atom may be exemplified by those disclosed in Japanese Patent Application Laid-open (Kokai) Nos. 11662/1992 and 166035/1999.

As the phenolic curing agent to be used as the component (B) according to the present invention, it is possible to use one of known and commonly used resins such as a phenol novolak resin, an alkylphenol novolak resin, a bisphenol A novolak resin, a dicyclopentadiene type phenol resin, a xylok type phenol resin, a terpene-modified phenol resin, and a polyvinylphenol, or a combination of two or more of the above compounds. Furthermore, the phenolic curing agent (B) may contain a nitrogen atom. The use of the phenolic curing agent improves uninflammability and adhesiveness. The phenolic curing agent containing a nitrogen atom may be exempified by a series of "Phenolite" 7050 manufactured by Dainippon Ink & Chemicals, Incorporated, which are novolak resins containing a triazine structure, and a melamine-modified phenol novolak resin manufactured by Yuka Shell K.K. With regard to the mixing amount of the

aforementioned phenol resin, it is desirable to mix 0.5 to 1.3 phenolic hydroxyl group equivalents of the phenol resin relative to one epoxy equivalent of the epoxy resin (A). Deviation from the range may result in the problem that thermal resistance of the resulting epoxy resin composition is deteriorated.

In order to attain good roughening with an oxidizing agent after curing under heating, the component (C) to be used according to the present invention is necessarily a phenoxy resin containing a bisphenol S skeleton and having a weight average molecular weight of 5,000 to 100,000. Furthermore, the phenoxy resin(C) preferably contains a bisphenol S skeleton and a bisphenol skeleton, and has a weight average molecular weight of 5,000 to 100,000. The phenoxy resin, because it contains a sulfone group, is less compatible with an epoxy resin, so that it is compatibly soluble in a varnish formed by dissolving the epoxy resin composition in a solvent, but an island structure is formed by phase separation in a cured product of an epoxy resin composition after curing under heating. Accordingly, it becomes possible to obtain a well-roughened surface without adding any roughening component. When the weight average molecular weight is less than 5,000, the effect of the phase separation cannot be attained, and when it exceeds 100,000, the phenoxy resin becomes hardly soluble in an organic solvent and therefore, cannot be used. The phenoxy resin is obtainable according to known and conventional methods such

as a method of reacting bifunctional epoxy resin with bisphenol S, a method of reacting a bisphenol S type epoxy resin with bisphenol, or the like. Among them, a phenoxy resin composed of a biphenyl type epoxy resin and bisphenol S has such characteristics that the resin itself has a high glass transition point as well as it affords a tight roughened surface. The mixing amount of the phenoxy resin (C) ranges from 5 to 50 parts by weight relative to 100 parts by weight in total of the epoxy resin (A) and the phenolic curing agent (B), and the most suitable amount is selected depending on the skeleton. The amount of less than 5% by weight is not preferred because of insufficient capability of being roughened, whereas the amount exceeding 50% by weight is also not preferred because of occurrence of phase separation of resin varnish itself or inversion of the island structure of a cured product. The phenoxy resin improves mechanical strength and flexibility of the cured coating film as well as it exhibits an effect of facilitating control of melt viscosity of the resin in an adhesive film and/or prepreg and an effect of prevention of repelling. In addition, it is possible to use the resin in combination with a binder polymer such as a usual phenoxy resin, a polyacrylate resin, a polyimide resin, a polyamidimide resin, a polycyanate resin, a polyester resin, or a thermosetting polyphenylene ether resin.

With regard to the curing accelerator to be used as the component (D) according to the present invention, it is

possible to use one of known and commonly used substances including an imidazole, a tertiary amine, a guanidine, or an epoxy adduct or a microcapsulated product thereof, and an organic phosphine compound such as triphenylphosphine or tetraphenyl phosphonium tetraphenyl borate, or a combination of two or more of the above substances. The mixing amount of the curing accelerator (D) is preferably in the range of 0.05 to 10 parts by weight relative to 100 parts by weight in total of the epoxy resin (A) and the phenolic curing agent (B). The amount of less than 0.05 parts by weight results in insufficient curing, whereas the amount exceeding 10 parts by weight is not effective for any further acceleration of curing, but rather results in the problem of deteriorating thermal resistance and/or mechanical strength. That is, with regard to the first embodiment of the present invention, preferred is an epoxy resin composition wherein 5 to 50 parts by weight of the phenoxy resin (C) and 0.05 to 10 parts by weight of the curing accelerator (D) are mixed with 100 parts by weight in total of the epoxy resin (A) and the phenolic curing agent (B).

The epoxy resin composition of the present invention may further contain a thermosetting resin and known and a commonly used additive in addition to the components described above. Examples of the thermosetting resin include a blocked isocyanate resin, a xylene resin, a radical initiator and a polymerizable resin, and the like. Examples of the additive include an inorganic filler such as

barium sulfate, barium titanate, a silicon oxide powder, amorphous silica, talc, clay, a mica powder, aluminum hydroxide, magnesium hydroxide, or the like; an organic filler such as a silicone powder, a nylon powder, a fluoride powder, or the like; a thickening agent such as asbestos, orben, bentone, or the like; a silicone type, fluoride type or macromolecule type defoaming and/or leveling agent; an adhesion improver such as an imidazole, a thiazole, a triazole, a silane coupling agent, or the like; and an additive such as a phosphorus flame retardant. It is also possible to use a known and commonly used coloring agent such as Phthalocyanine Blue, Phthalocyanine Green, Iodine Green, Disazo Yellow, titanium oxide, carbon black, or the like, if necessary.

The second embodiment of the present invention relates to an adhesive film obtainable by forming a thin film of the epoxy resin composition on a supporting base film. The process for manufacturing an adhesive film comprises applying a resin varnish, wherein the resin composition has been dissolved in a prescribed solvent, on the surface of a supporting base film which is used as a support, and evaporating the solvent through heating and/or exposing to a hot air blast to form a thin film. The supporting base film may be exemplified by a polyolefin such as polyethylene, polyvinyl chloride, or the like, a polyester such as polyethylene terephthalate, or the like, a polycarbonate, a polyimide, a release paper, or a metal foil

such as copper foil or aluminum foil. The supporting base film is able to have been subjected to mat treatment and corona treatment as well as peelable treatment. As the organic solvent, it is possible to use one of ordinary solvents including ketones such as acetone, methyl ethyl ketone, cyclohexanone and the like, esters of acetic acid such as ethyl acetate, butyl acetate, cellosolve acetate, propylene glycol monomethyl ether acetate, carbitol acetate and the like, cellosolves such as cellosolve, butyl cellosolve and the like, carbitols such as carbitol, butyl carbitol and the like, aromatic hydrocarbons such as toluene, xylene and the like, dimethylformamide, dimethylacetamide, and the like, or a combination of two or more of the above solvents. More specifically, the adhesive film is the film formed by laminating a supporting base film having a thickness of 10 to 200 μm with an epoxy resin composition layer having a thickness of the range of 10 to 150 μm, which should not be less than the thickness of a conductor layer of the internal-layer circuit board to be laminated, and further laminating the other surface of the resin layer with a protective film such as a supporting film having a thickness of 1 to 40 μm, and the resulting film is stored with winding up to a roll.

With regard to the third embodiment of the present invention, the prepreg can be prepared by coating and/or impregnating a sheet-shape reinforced base material made of a fiber with the epoxy resin composition according to a hot-

melt method or a solvent method, and heating to semi-cure the composition. As the sheet-shape reinforced base material made of a fiber, it is possible to use a known and commonly used fiber for a prepreg such as glass cloth or aramide fiber. Among hot-melt methods, there are known, for example, a method of temporarily coating a coated paper easily releasable from a resin with a solvent-free resin composition and laminating it, and a method of directly coating a solvent-free resin composition with a die coater. The solvent method includes the steps of dipping the sheet-shape reinforced base material in a resin varnish wherein the epoxy resin composition has been dissolved in an organic solvent, to impregnate the material with the resin varnish, and then drying it to obtain a prepreg.

The fourth embodiment of the present invention relates to a multilayer printed-wiring board wherein a plated conductor layer is formed on the roughened surface of a cured product of the epoxy resin composition while the other surface is closely laminated onto a patterned internal-layer circuit board.

The following will explain a process for manufacturing a multilayer printed-wiring board using an epoxy resin composition of the present invention. The epoxy resin composition of the present invention is first coated on a patterned internal-layer circuit board, and cured under heating, after drying when it contains an organic solvent. The internal-layer circuit board may be a glass/epoxy

laminate, a metal board, a polyester board, a polyimide board, a BT resin board, a thermosetting polyphenylene ether board, or the like, and the surface of the circuit is able to have been subjected to roughening treatment in advance. The drying is preferably carried out at 70 to 130°C for 5 to 40 minutes. The heat-curing is preferably carried out under heating at 130 to 180°C for 15 to 90 minutes. After the curing under heating, necessary through holes or via holes are made by a drill and/or a laser or plasma. Then, roughening treatment is given with an oxidizing agent such as a permanganate, a bichromate, ozone, hydrogen peroxide/sulfuric acid, nitric acid, or the like, to form protrusive anchors on the surface of the adhesive layer. Then, a conductor layer is formed by nonelectrolytic and/or electrolytic plating. At this time, when a plated resist having the pattern reverse to that of the conductor layer is formed in advance, the conductor layer may be formed simply by nonelectrolytic plating. After the conductor layer has been thus formed, by annealing it at 150 to 180°C for 20 to 60 minutes, any residual unreacted epoxy resin can be cured to enhance the peeling strength of the conductor layer to a further extent.

With regard to the sixth embodiment of the present invention, the above-described adhesive film is laminated on a patterned internal-layer circuit board for manufacturing a multilayer printed-wiring board using an adhesive film composed of the epoxy resin composition of the present

invention, the supporting base film, and, if necessary, a protective film. After removing the protective film in the case where a protective film is present, the lamination is carried out by sticking the thin film of the epoxy resin composition having a property of an adhesive on the circuit board with pressurizing and heating. It is preferable to carry out the lamination at a pressing temperature of 70 to 130°C and a pressing pressure of 1 to 11 kgf/cm^2 under reduced pressure after preheating the film and the internal-layer circuit board, if necessary. The lamination may be carried out by a process either batchwise or continuously by means of a roll. After the lamination, the resulting laminate is cooled to around room temperature. Then, the supporting film is detached to transfer the epoxy resin composition on the internal-layer circuit board, and the composition is cured under heating. In the case where a supporting film which has been subjected to peelable treatment is used, the supporting film may be detached after the curing under heating. Thereafter, similarly to the method described above, a multilayer printed-wiring board can be manufactured by roughening the surface of the film with an oxidizing agent and forming a conductor layer on the roughened surface by plating.

On the other hand, for manufacturing a multilayer printed-wiring board using a prepreg composed of the epoxy resin composition of the present invention, firstly, one sheet or, if necessary, several sheets of the prepreg are

stacked on a patterned internal-layer circuit board, put between metal plates with intervening release films, and then pressed under conditions of pressurizing and heating. The shaping is preferably carried out under a pressure of 5 to 40 kgf/cm^2 at a temperature of 120 to 180°C for 20 to 100 minutes. It is also possible to manufacture an intermediate product for the same purpose according to the aforementioned lamination process. Thereafter, similarly to the method described above, a multilayer printed-wiring board can be manufactured by roughening the surface of the prepreg with an oxidizing agent and forming a conductor layer on the roughened surface by plating. When the internal-layer circuit board has two or more layers of a patterned internal-layer circuit in the same direction, the multilayer printed-wiring board thus manufactured will possess insulating layer(s) of the cured product of the epoxy resin composition according to any one of claims 1 to 5 between the internal-layer circuits. "A patterned internal-layer circuit" named in the present invention is a relative name toward "a multilayer printed-wiring board". For example, after circuits are formed on both the surfaces of a substrate board and cured thin films of the epoxy resin composition are further formed as insulating layers on the surfaces of both the circuits, a four-layer printed-wiring board can be formed by further formation of circuits on both the resulting surfaces. In this case, an internal-layer circuit board means a printed-wiring board wherein circuits

are formed on both the surfaces of a substrate board. Furthermore, when one more layer of a circuit is additionally formed on each of both the surfaces of the four-layer printed-wiring board with an intervening insulating layer, a six-layer printed-wiring board results. In this case, an internal-layer circuit board means the aforementioned four-layer printed-wiring board.

The fifth embodiment invention of the present invention relates to a multilayer printed-wiring board manufactured according to the above-described sixth embodiment of the present invention, and more particularly, it relates to a multilayer printed-wiring board which is obtainable by the steps of coating a patterned internal-layer circuit board with the above-described epoxy resin composition, curing it under heating, roughening the surface of the cured resin composition with an oxidizing agent, and forming a conductor layer on the roughened surface by plating; a multilayer printed-wiring board which is obtainable by the steps of laminating the above-described adhesive film on a patterned internal-layer circuit board under conditions of pressurizing and heating, detaching the supporting base film if necessary, curing the epoxy resin composition under heating, roughening the surface of the cured resin composition layer with an oxidizing agent, and forming a conductor layer on the roughened surface by plating; and a multilayer printed-wiring board which is obtainable by the steps of laminating the above-described

prepreg on a patterned internal-layer circuit board under conditions of pressurizing and heating to integrate them, roughening the surface of the prepreg with an oxidizing agent, and forming a conductor layer on the roughened surface by plating.

With regard to the seventh embodiment of the present invention, the following will describe a process for manufacturing a laminate which is obtainable by the steps of coating the surface formed by etching out a copper foil of a copper foil-clad laminate on both sides or at least one surface of an unclad laminate with the above-described epoxy resin composition, and curing it under heating; a laminate which is obtainable by the steps of laminating the above-described adhesive film on the surface formed by etching out a copper foil of a copper foil-clad laminate on both sides or at least one surface of an unclad laminate under conditions of pressurizing and heating, detaching the supporting base film, if necessary, and curing it under heating; a laminate which is obtainable by laminating the above-described prepreg on the surface formed by etching out a copper foil of a copper foil-clad laminate on both sides or at least one surface of an unclad plate under conditions of pressurizing and heating; and a laminate which is obtainable by laminating the above-described prepreg under conditions of pressurizing and heating.

A laminate is obtainable by coating the surface formed by etching out a copper foil of a copper foil-clad

laminate on both sides or at least one surface of an unclad laminate with the above-described epoxy resin composition of the present invention, and curing it under heating. The aforementioned unclad laminate is obtainable by using a release film or the like instead of a copper-foil upon manufacturing the copper foil-clad laminate. The laminate thus obtained is subjected to roughening treatment with an oxidizing agent such as a permanganate, a bichromate, ozone, hydrogen peroxide/sulfuric acid, or nitric acid to form protrusive anchors on the surface of the laminate. Then, a conductor layer can be directly formed on the surface of the laminate by nonelectrolytic and/or electrolytic plating.

A laminate is also obtainable by laminating an adhesive film composed of the epoxy resin composition of the present invention on the surface formed by etching out a copper foil of a copper foil-clad laminate on both sides or at least one surface of an unclad laminate, and curing it under heating. The laminate thus obtained is subjected to a roughening treatment with an oxidizing agent such as a permanganate, a bichromate, ozone, hydrogen peroxide/sulfuric acid, or nitric acid to form protrusive anchors on the surface of the laminate. Then, a conductor layer can be directly formed on the surface of the laminate by nonelectrolytic and/or electrolytic plating.

A laminate is obtainable by stacking a prescribed number of sheets of the prepreg composed of the epoxy resin composition of the present invention or placing it on a

surface formed by etching out a copper foil of a copper foil-clad laminate on both sides or at least one surface of an unclad laminate, putting the resulting stack or laminate between metal plates with intervening release films, and then pressing under conditions of pressurizing and heating. The laminate thus obtained is subjected to roughening treatment with an oxidizing agent such as a permanganate, a bichromate, ozone, hydrogen peroxide/sulfuric acid, or nitric acid to form protrusive anchors on the surface of the laminate. Then, a conductor layer can be directly formed on the surface of the laminate by nonelectrolytic and/or electrolytic plating.

EXAMPLES

The present invention will be explained more specifically with reference to Examples, Comparative Examples, Manufacturing Examples, and Comparative Manufacturing Examples, but the present invention is not limited thereby.

[Example 1] An epoxy resin composition was prepared by dissolving 20 parts by weight (hereinafter, the mixing amounts being all expressed in parts by weight) of a bisphenol A type epoxy resin ("Epicoat 828" manufactured by Yuka Shell Epoxy K.K., and having an epoxy equivalent of 185) and 45 parts of a cresol novolak type epoxy resin

("EPICLON N-673" manufactured by Dainippon Ink & Chemicals, Incorporated, and having an epoxy equivalent of 215) as the component (A) and 30 parts of a phenol novolak resin ("Phenolite" manufactured by Dainippon Ink & Chemicals, Incorporated, and having a phenolic hydroxyl equivalent of 105) as the component (B) in 20 parts of ethyl diglycol acetate and 20 parts of solvent naphtha under heating with stirring, followed by cooling the resulting mixture to room temperature, and adding thereto 30 parts of a cyclohexanone varnish of a phenoxy resin composed of the "828" and bisphenol S ("YL6747H30" manufactured by Yuka Shell Epoxy K.K., containing 30% by weight of nonvolatile matter and having a weight average molecular weight of 47000) as the component (C), and 0.8 parts of a crushed product of 2-phenyl-4,5-bis(hydroxymethyl)imidazole as the component (D), as well as 2 parts of finely divided silica and 0.5 parts of a silicone type defoaming agent.

[Example 2] An epoxy resin composition was prepared by dissolving 20 parts of a bisphenol A type epoxy resin ("Epicoat 828" manufactured by Yuka Shell Epoxy K.K.), and 45 parts of a phosphorus-containing epoxy resin described in Synthetic Example 1 of Japanese Patent Application Laid-open (Kokai) No. 166035/1999 (epoxy equivalent of 300, and phosphorus content of 2.0% by weight) as the component (A) in methyl ethyl ketone (hereinafter, referred to as MEK) under heating with stirring, followed by

cooling the resulting mixture to room temperature, and adding thereto 50 parts of a MEK varnish of a phenol novolak resin containing a triazine structure ("Phenolite LA-7052" manufactured by Dainippon Ink & Chemicals, Incorporated, containing 60% of nonvolatile matter and having a phenolic hydroxyl equivalent of 120) as the component (B), 70 parts of a cyclohexanone varnish of a phenoxy resin composed of a tetramethyl type biphenyl epoxy resin ("YX-4000" manufactured by Yuka Shell Epoxy K.K.) and bisphenol S ("YL6746H30" manufactured by Yuka Shell Epoxy K.K. containing 30% by weight of nonvolatile matter, and having a weight average molecular weight of 30000) as the component (C), and 0.5 parts of a crushed product of 2,4-diamino-6-(2-methyl-1-imidazolylethyl)-1,3,5-triazine•isocyanurate adduct as the component (D), as well as 2 parts of finely divided silica. The epoxy resin composition as prepared in the varnish form was applied by a roller coater onto a PET film having a thickness of 38 μm in such amount that the resulting layer should have a thickness of 60 μm after dried, and was dried at 80 to 120°C for 10 minutes, whereby an adhesive film was obtained.

[Example 3] An epoxy resin composition was prepared by dissolving 15 parts of a cresol novolak type epoxy resin ("EPICLON N-673" manufactured by Dainippon Ink & Chemicals, Incorporated), and 50 parts of a phosphorus-containing epoxy resin described in Synthetic Example 1 of

Japanese Patent Application Laid-open (Kokai) No. 166035/1999 (epoxy equivalent of 300, and phosphorus content of 2.0% by weight) as the component (A) in MEK under heating with stirring, followed by cooling the resulting mixture to room temperature, adding thereto 45 parts of an MEK varnish of a phenol novolak resin containing a triazine structure ("Phenolite LA-7052" manufactured by Dainippon Ink & Chemicals, Incorporated) as the component (B), 50 parts of a cyclohexanone varnish of a phenoxy resin composed of a tetramethyl type biphenyl epoxy resin and bisphenol S ("YL6746H30" manufactured by Yuka Shell Epoxy K.K.) as the component (C), and 0.5 parts of a crushed product of 2,4-diamino-6-(2-methyl-1-imidazolylethyl)-1,3,5-triazine•isocyanurate adduct as the component (D), as well as 20 parts of a phenoxy resin varnish ("YP-50-EK35" manufactured by Tohto Kasei Co., Ltd.) and 2 parts of finely divided silica. An aramide fiber cloth ("Technola" manufactured by Teijin Limited) was impregnated with the epoxy resin composition as prepared in the varnish form and the impregnated was dried at 150°C, whereby a prepreg having a resin content of about 45% by weight and a thickness of 0.1 mm was obtained.

[Example 4] A glass cloth of 100 μm in thickness was impregnated with the epoxy resin composition described in Example 2 and the impregnated was dried at 80 to 120°C for 10 minutes, whereby a prepreg having a resin content of

40% was obtained.

[Example 5] A glass cloth of 34 μm in thickness was impregnated with the epoxy resin composition described in Example 2 and the impregnated was dried at 80 to 120°C for 10 minutes, whereby a prepreg having a resin content of 75% was obtained.

[Comparative Example 1] An epoxy resin composition was prepared by dissolving 20 parts by weight of a bisphenol A type epoxy resin ("Epicoat 828" manufactured by Yuka Shell Epoxy K.K.) and 45 parts of a cresol novolak type epoxy resin ("EPICLON N-673" manufactured by Dainippon Ink & Chemicals, Incorporated) as the component (A) and 30 parts of a phenol novolak resin ("Phenolite" manufactured by Dainippon Ink & Chemicals, Incorporated) as the component (B) in 20 parts of ethyl diglycol acetate and 20 parts of solvent naphtha under heating with stirring, followed by cooling the resulting mixture to room temperature, adding thereto 30 parts of a phenoxy resin varnish ("YP-50-EK35" manufactured by Tohto Kasei Co., Ltd.), and 0.8 parts of a crushed product of 2-phenyl-4,5-bis(hydroxymethyl)imidazole as the component (D), as well as 2 parts of finely divided silica and 0.5 parts of a silicone type defoaming agent.

[Comparative Example 2] An epoxy resin composition was prepared by dissolving 20 parts of a bisphenol A type

epoxy resin ("Epicoat 828" manufactured by Yuka Shell Epoxy K.K.), and 45 parts of a phosphorus-containing epoxy resin described in Synthetic Example 1 of Japanese Patent Application Laid-open (Kokai) No. 166035/1999 (epoxy equivalent of 300, and phosphorus content of 2.0% by weight) as the component (A) in MEK under heating with stirring, followed by cooling the resulting mixture to room temperature, adding thereto 50 parts of an MEK varnish of a phenol novolak resin containing a triazine structure ("Phenolite LA-7052" manufactured by Dainippon Ink & Chemicals, Incorporated) as the component (B), 15 parts of end-epoxidated polybutadiene rubber ("Denarex R-45EPT" ex Nagase Chemicals Ltd.), 15 parts of calcium carbonate, 30 parts of a phenoxy resin varnish ("YP-50-EK35" manufactured by Tohto Kasei Co., Ltd.), and 0.5 parts of a crushed product of 2,4-diamino-6-(2-methyl-1-imidazolylethyl)-1,3,5-triazine•isocyanurate adduct as the component (D), as well as 2 parts of finely divided silica. The epoxy resin composition as prepared in the varnish form was applied by a roller coater onto a PET film having a thickness of 38 μm in such amount that the resulting layer should have a thickness of 60 μm after dried, and was dried at 80 to 120°C for 10 minutes, whereby an adhesive film was obtained.

[Manufacturing Example 1] An internal-layer circuit board was formed from a glass/epoxy laminate clad on both sides with a copper foil having a thickness of 35 μm,

and the epoxy resin composition obtained in Example 1 was applied thereon by screen printing and dried at 120°C for 10 minutes. Then, the composition was also applied on the reverse side and dried similarly, and cured under heating at 170°C for 30 minutes. Thereafter, the necessary through holes or via holes were made with a drill and/or a laser, and after roughening the surface of the resin layer with an alkaline oxidizing agent of a permanganate (a reagent solution manufactured by Atotech Japan Co., Ltd.), nonelectrolytic and/or electrolytic plating was performed and a four-layer printed-wiring board was obtained in accordance with a subtractive process. Then, the board was further subjected to an annealing treatment by heating at 170°C for 30 minutes.

[Manufacturing Example 2] An internal-layer circuit board was formed from a glass/epoxy laminate clad on both sides with a copper foil having a thickness of 35 μm, and the adhesive film obtained in Example 2 was laminated on both sides of the board with a vacuum laminator at a temperature of 110°C, a pressure of 1 kgf/cm^2 and an atmospheric pressure of 5 mmHg or below, and then the PET film was detached, followed by curing the resin composition under heating at 170°C for 30 minutes. Thereafter, the necessary through holes or via holes were made with a drill and/or a laser, followed by roughening the surface of the film with an alkaline oxidizing agent of a permanganate,

nonelectrolytic and/or electrolytic plating was performed and a four-layer printed-wiring board was obtained in accordance with a subtractive process. Then, the board was further subjected to an annealing treatment by heating at 150°C for 30 minutes.

[Manufacturing Example 3] An internal-layer circuit board was formed from a glass/epoxy laminate clad on both sides with a copper foil having a thickness of 35 μm, and one sheet of the prepreg obtained in Example 3 was stacked on each of both the sides thereof and the stack was placed between metal plates with intervening release films, and then pressed at a temperature of 120°C and a pressure of 10 kgf/cm^2 for 10 minutes and then at a temperature of 170°C and a pressure of 40 kgf/cm^2 for 60 minutes. Thereafter, the necessary through holes or via holes were made with a drill and/or a laser, followed by roughening the surface with an alkaline oxidizing agent of a permanganate, conductor layers were formed over the whole surface by nonelectrolytic and/or electrolytic plating and a four-layer printed-wiring board was obtained in accordance with a subtractive process.

[Comparative Manufacturing Example 1] A four-layer printed-wiring board was obtained in the same manner as in Manufacturing Example 1 using the epoxy resin composition obtained in Comparative Example 1.

[Comparative Manufacturing Example 2] A four-layer printed-wiring board was obtained in the same manner as in Manufacturing Example 2 using the epoxy resin composition obtained in Comparative Example 2.

With regard to the four-layer printed-wiring boards obtained in Manufacturing Examples 1 to 3 and Comparative Manufacturing Examples 1 and 2, SEM photographs of the surfaces of the cured resin composition after roughening are shown in Figure 1, and the results of measurement of conductor peel strength and heat resistance at boiling point are shown in Table 1.

Table 1

	Peel strength (kgf/cm)	Heat-resistance at boiling point
Manufacturing Ex. 1	0.90	○
Manufacturing Ex. 2	1.1	○
Manufacturing Ex. 3	1.0	○
Comparative Manufact. Ex. 1	0.25	×
Comparative Manufact. Ex. 2	0.30	×

Measurement of peel strength: The measurement was performed according to JIS C6481. Thickness of a plated conductor was about 30 μm.

Heat-resistance at boiling point: The four-layer printed-wiring boards obtained were evaluated by boiling treatment for 2 hours, followed by dipping them in a solder bath at 260°C for 30 seconds. Evaluation was carried out by

judging the appearance of the test boards with the eye. In the table, O means good, whereas × means occurrence of blister, peeling or measling.

From the results of Examples 1 to 3 and Manufacturing Examples 1 to 3, it was found that according to the process of the present invention, a copper plating excellent in adhesiveness was formed through roughening with an oxidizing agent and high thermal resistance was also attained, so that a highly reliable multilayer printed-wiring board could be manufactured by a build-up type technique. Particularly, the resin composition wherein the epoxy resin (A) contained a phosphorus atom, the phenolic curing agent (B) contained a nitrogen atom, and the phenoxy resin (C) contained a bisphenol S skeleton and a biphenyl skeleton, was found to be suitable for fine pattern formation owing to high peel strength and formation of minuter anchors upon roughening. On the other hand, in the case of Comparative Example 1 where the essential component (C) of the present invention was not used, protrusion exhibiting a sufficient anchoring effect was not formed by the action of an oxidizing agent, so that peel strength of the copper plating was found to be poor. Furthermore, in the case where an epoxy resin containing a phosphorus atom was used as in Comparative Example 2, the roughened surface was bad in shape even when a roughening component was contained and adhesion of the copper plating was poor, so

that the resulting board had an inferior thermal resistance at boiling point and therefore, was not suitable for practical use.

[Manufacturing Example 4] A laminate was formed by etching out the copper foil of a glass/epoxy laminate clad on both sides with a copper foil having a thickness of 18 μm, stacking one sheet of the prepreg obtained in Example 5 on each of both the sides, laminating the prepreg on both the sides with a vacuum laminator with intervening release films at a temperature of 110°C, a pressure of 1 kgf/cm^2 and an environmental pressure of 5 mmHg or below, detaching the release films and curing under heating at 170°C for 60 minutes. Thereafter, the surface was roughened with an alkaline oxidizing agent of a permanganate, and conductor layers of about 30 μm were formed by nonelectrolytic and/or electrolytic plating over the whole surface. The peel strength was 1.0 kgf/cm.

[Manufacturing Example 5] A laminate having a thickness of 0.2 mm was formed by stacking two sheets of the prepreg obtained in Example 4, placing the stack between metal plates with intervening release films, and pressing the whole at a temperature of 120°C and a pressure of 10 kgf/cm^2 for 15 minutes and then at a temperature of 170°C and a pressure of 40 kgf/cm^2 for 60 minutes. Table 2 shows the properties of the resulting laminate. Thereafter, the

surface was roughened with an alkaline oxidizing agent of a permanganate, and conductor layers of about 25 µm in thickness were formed by nonelectrolytic and/or electrolytic plating over the whole surface. The peel strength was 0.9 kgf/cm.

Table 2

Properties		of Laminate
CTE(ppm)	x-y	10.6
	z	56
Dielectric constant	1MHz	4.81
	500MHz	4.4
	1GHz	4.37
Dielectric tangent	1MHz	0.026
	500MHz	0.023
	1GHz	0.022
Tensile strrength (kgf/mm^2)		27.4
Breaking elongation percentage (%)		2.8
Bending strength (kgf/mm^2)		
	longitudinal	49
	lateral	50.3
Bending elasticity	longitudinal	1749
	lateral	1930

[Effects of the Invention]

According to the process of the present invention, it is possible to form a conductor layer excellent in adhesiveness suitable for fine pattern formation without requiring, in the insulating layer, a roughening component which deteriorates performance, in manufacturing a multilayer printed-wiring board of the build-up type.

CLAIMS

1. An epoxy resin composition comprising, as the essential components, (A) an epoxy resin having two or more epoxy groups in one molecule, (B) a phenolic curing agent, (C) a phenoxy resin containing a bisphenol S skeleton and having a weight average molecular weight of 5,000 to 100,000, and (D) a curing accelerator.

2. The epoxy resin composition according to claim 1, wherein the epoxy resin (A) contains a phosphorus atom.

3. The epoxy resin composition according to claim 1 or 2, wherein the phenolic curing agent (B) contains a nitrogen atom.

4. The epoxy resin composition according to any of claims 1 to 3, wherein the phenoxy resin (C) contains a bisphenol S skeleton and a biphenyl skeleton, and has a weight average molecular weight of 5,000 to 100,000.

5. The epoxy resin composition according to any one of claims 1 to 4, wherein 5 to 50 parts by weight of the phenoxy resin (C) and 0.05 to 10 parts by weight of the curing accelerator (D) are mixed with 100 parts by weight in total of the epoxy resin (A) and the phenolic curing agent (B).

6. An adhesive film which is obtainable by forming a thin film of the epoxy resin composition according to any one of claims 1 to 5 on a supporting base film.

7. A prepreg which is obtainable by coating and/or impregnating a sheet-shape reinforced base material made of

a fiber with the epoxy resin composition according to any one of claims 1 to 5.

8. A multilayer printed-wiring board wherein a plated conductor layer is formed on the roughened surface of a cured product of the epoxy resin composition according to any one of claims 1 to 5 while the other surface is closely laminated onto a patterned internal-layer circuit board.

9. A multilayer printed-wiring board which is obtainable by the steps of (a) coating a patterned internal-layer circuit board with the epoxy resin composition according to any one of claims 1 to 5, (b) curing it under heating, (c) roughening the surface of the cured product with an oxidizing agent, and (d) forming a conductor layer on the roughened surface by plating.

10. A multilayer printed-wiring board which is obtainable by the steps of (a) laminating the adhesive film according to claim 6 on a patterned internal-layer circuit board under conditions of pressurizing and heating, (b) detaching the supporting base film, if necessary, (c) curing the epoxy resin composition under heating, (d) roughening the surface of the cured product with an oxidizing agent, and (e) forming a conductor layer on the roughened surface by plating.

11. A multilayer printed-wiring board which is obtainable by the steps of (a) laminating the prepreg according to claim 7 on a patterned internal-layer circuit board under conditions of pressurizing and heating to

integrate them, (b) roughening the surface of the prepreg with an oxidizing agent, and (c) forming a conductor layer on the roughened surface by plating.

12. A process for manufacturing a multilayer printed-wiring board comprising the steps of (a) coating a patterned internal-layer circuit board with the epoxy resin composition according to any one of claims 1 to 5, (b) curing it under heating, (c) roughening the surface of the cured composition with an oxidizing agent, and (d) forming a conductor layer on the roughened surface by plating.

13. A process for manufacturing a multilayer printed-wiring board comprising the steps of (a) laminating the adhesive film according to claim 6 on a patterned internal-layer circuit board under conditions of pressurizing and heating, (b) detaching the supporting base film, if necessary, (c) curing the epoxy resin composition under heating, (d) roughening the surface of the cured product with an oxidizing agent, and (e) forming a conductor layer on the roughened surface by plating.

14. A process for manufacturing a multilayer printed-wiring board comprising the steps of (a) laminating the prepreg according to claim 7 on a patterned internal-layer circuit board under conditions of pressurizing and heating to integrate them, (b) roughening a surface of the prepreg with an oxidizing agent, and (c) forming a conductor layer on the roughened surface by plating.

15. A laminate which is obtainable by the steps of

(a) coating the surface formed by etching out a copper foil of a copper foil-clad laminate on both sides or at least one surface of an unclad laminate with the epoxy resin composition according to any one of claims 1 to 5, and (b) curing it under heating.

16. A laminate which is obtainable by the steps of (a) laminating the adhesive film according to claim 6 on the surface formed by etching out a copper foil of a copper foil-laminated clad on both sides or at least one surface of an unclad laminate under conditions of pressurizing and heating, (b) detaching the supporting base film, if necessary, and (c) curing it under heating.

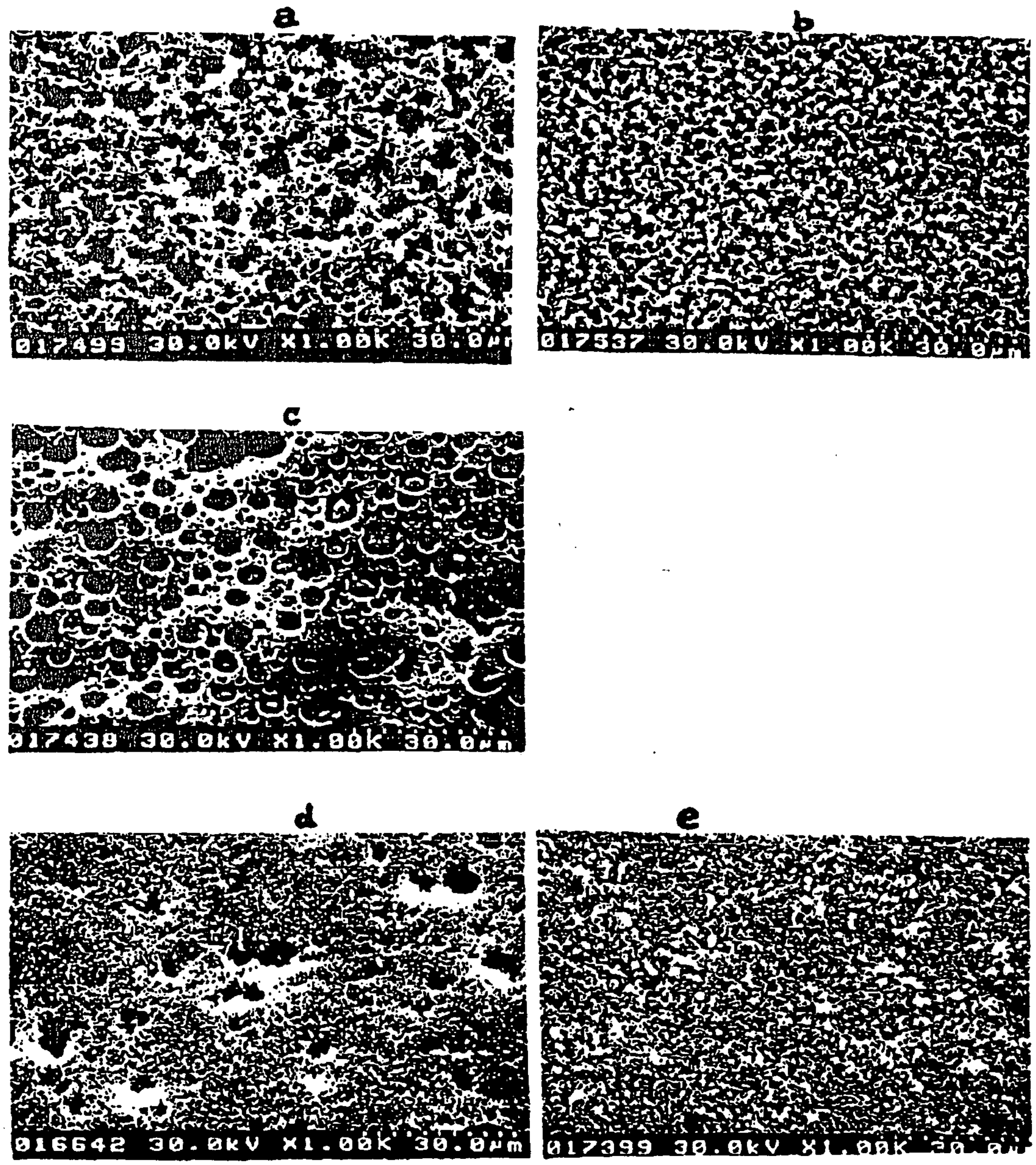
17. A laminate which is obtainable by laminating the prepreg according to claim 7 on the surface formed by etching out a copper foil of a copper foil-laminated clad on both sides or at least one surface of an unclad plate under conditions of pressurizing and heating.

18. A laminate which is obtainable by laminating the prepreg according to claim 7 under conditions of pressurizing and heating.

ABSTRACT

Here are disclosed an epoxy resin composition comprising, as essential components, (A) an epoxy resin having two or more epoxy groups in one molecule, (B) a phenolic curing agent, (C) a phenoxy resin containing a bisphenol S skeleton and having a weight average molecular weight of 5,000 to 100,000, and (D) a curing accelerator, particularly preferred being the epoxy resin composition wherein the epoxy resin (A) contains a phosphorus atom, the phenolic curing agent (B) contains a nitrogen atom, and the phenoxy resin (C) contains a bisphenol S skeleton and a biphenyl skeleton, an adhesive film formed by coating the above epoxy resin composition of the present invention on a supporting base film, and a prepreg obtainable by coating and/or impregnating a sheet-shape reinforced base material made of a fiber with the resin composition, as well as a multilayer printed-wiring board made by using them and a process for manufacturing the same, whereby the object may be realized of providing an epoxy resin composition which enables to form a conductor layer excellent in adhesiveness without requiring, in the insulating layer, a roughening component which deteriorates performance, as well as a multilayer printed-wiring board using it and a process for manufacturing the same, in a multilayer printed-wiring board of a build-up type which is formed by stacking alternately conductor circuitry layers and insulating layers.

Fig. 1


a
017499 30.0kV X1.00k 30.0µm
b
017537 30.0kV X1.00k 30.0µm
c
017438 30.0kV X1.00k 30.0µm
d
016642 30.0kV X1.00k 30.0µm
e
017399 30.0kV